

## sp magnetism in clusters of gold thiolates

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**Abstract.** Using first-principles calculations, we consider the bond between thiolate and small Au clusters, with particular emphasis on the resulting magnetic moment. The moment of pure gold clusters is  $1 \mu_B$  for clusters with an odd number of Au atoms and zero for those with an even number. The addition of the thiolate, having an odd number of electrons itself, shifts the phase of the odd–even oscillations so that particles with an even number of Au atoms now have unit moment. Surprisingly, gold thiolate exhibits a dramatic and non-intuitive distribution of charge and spin moment. Our results show that the S–Au bond is such that sulfur does not get charge and an electron is transferred to the Au cluster. This extra electron is mainly sp in character and resides in an electronic shell below the Au surface. The calculations suggest that any thiolate-induced magnetism occurs in the gold nanoparticle and not the thiolate, and can be controlled by modifying the thiolate coverage.

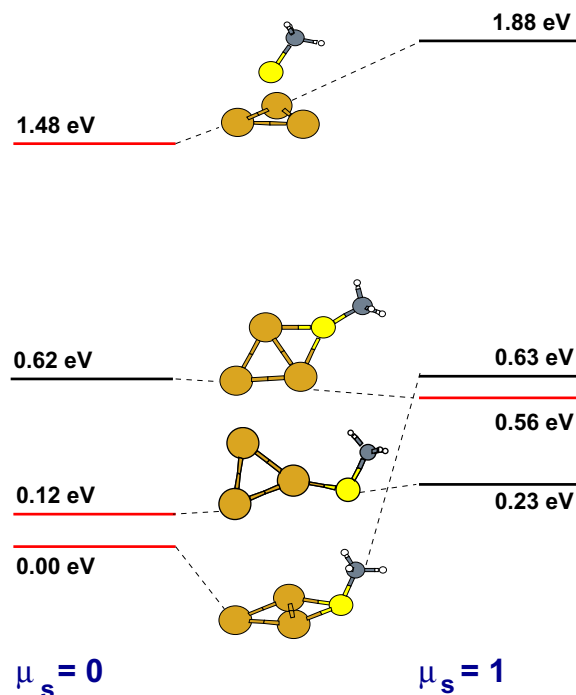
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Nanoparticles consisting of metals and oxides have been shown to exhibit magnetic behavior even when they are composed only of non-magnetic compounds [1–5]. When organic molecules are attached to Au via thiol bonds, Au nanoparticles (NPs) with a size of about 1.6 nm show a kind of ferromagnetic response, even at room temperature. The saturation magnetization is very low, being typically in the range  $10^{-1}$ – $10^{-2}$  Bohr magnetons per atom, and is weakly dependent on temperature in the range from 4 K up to room temperature. The small magnetic moment is not caused by the few magnetic impurities present, because any increase in the number of impurities causes the magnetic signal to disappear [3]. The results of both x-ray magnetic circular dichroism (XMCD) and Au Mössbauer spectroscopy have shown that the Au atom possesses a magnetic moment [4, 5], which was thought to be due to the spins of Au d-holes introduced by the ligands [6]. However, the observed saturation at room temperature and the shape of the magnetization curve still lack a convincing explanation. A more detailed understanding of the nature of the gold–alkenethiol bond is therefore required. In particular, the understanding of the interaction between alkenethiols and Au NPs is one of the main challenges in the study of their magnetic structure.

Theory and experiments have shown that the coverage of the magic gold clusters by thiols with well-defined compositions [7–10] is rather complicated. Sulfur atoms are attached with a single bond to a gold atom of the cluster [11, 12]. These magic or closed-shell clusters are highly ordered arrangements with full electronic sp shells, as in noble metal clusters in general [13]. Additionally, alkenethiols with longer chains on Au surfaces have been the focus of detailed theoretical studies [14] and the presence of several different metastable states are known. In these cases, the sulfur atoms in the gold layers become arranged in a bridge configuration for the ground state. A range of different coordination numbers between thiols and gold must therefore be considered in any investigation. Although there have been a number of studies of the changes in the geometrical structure induced by alkenethiols on gold surfaces and closed-shell gold clusters [9], to our knowledge no studies have so far focused on the magnetism of the NPs covered by such molecules by increasing the number of gold atoms to see the effect of open shells.

The singly or doubly occupied highest occupied molecular orbital (HOMO) levels of the pure Au clusters are responsible for the odd–even oscillations, which are otherwise rather independent of the number of atoms in the cluster. We have therefore chosen to investigate the interaction between alkenethiols  $-\text{SCH}_3$  and minimal gold clusters. The interactions of gold clusters with thiols are considered to be a suitable model of adsorption of thiols onto larger NPs [9].

Calculations used the Amsterdam density functional (ADF) code [15], which implements an all-electron local-orbitals scheme based on density functional theory (DFT). The valence states were taken to be the gold 5p, 4f, 5d and 6s and the sulfur, carbon and hydrogen states, and were expanded in quadruple zeta with two polarization functions per atom. The relativistic effects of gold were modeled using the zeroth-order regular approximation (ZORA) to the Dirac equation; for details see [16] and references therein; its scalar relativistic version was used for the structural optimizations. The optimization of the geometry was carried out until the forces were all smaller than  $0.002 \text{ eV } \text{\AA}^{-1}$ . The criterion to stop the electronic self-consistency is that the commutator between the Fock and density matrices gets below  $10^{-6}$ . The generalized gradient approximation (GGA) of Perdew–Burke–Ernzerhof [17] was used to treat exchange

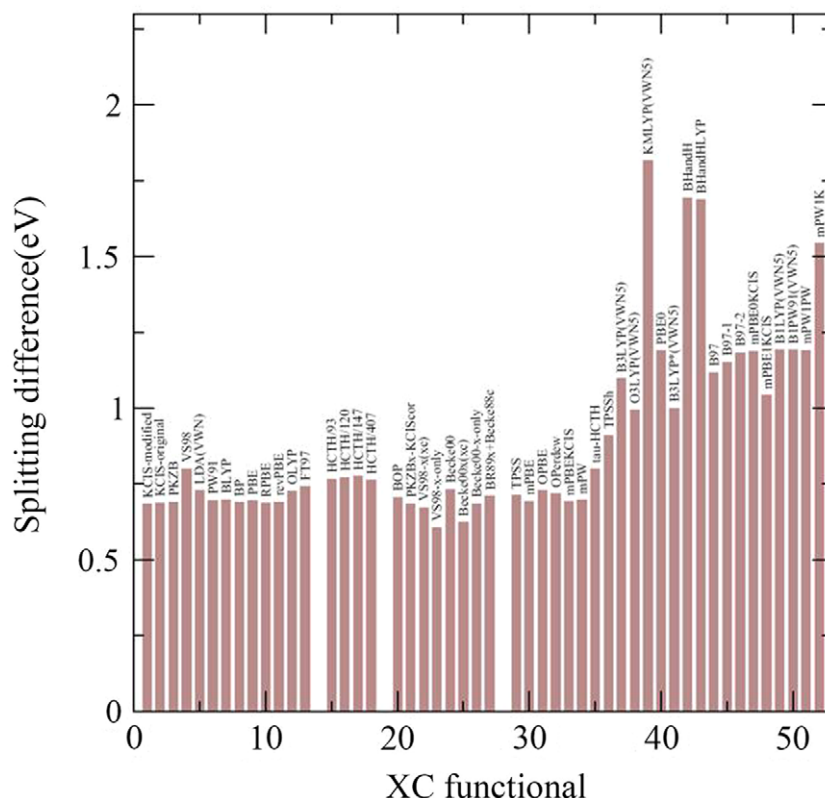


**Figure 1.** DFT energies for various states of spin magnetic moments and thiol–Au<sub>3</sub> configurations. The energies refer to the spin and geometry of the ground state. In order of size, the atoms are gold, sulfur, carbon and hydrogen. Note the different types of Au–sulfur bonds.

and correlation. The magnetic anisotropy (MAE) was obtained from self-consistent ZORA relativistic calculations including spin–orbit. The resulting GGA data were regarded as a lower estimate for the MAE. An orbital polarization correction (OPC) [18] should be considered in order to obtain an estimate of the MAE, beyond the actual scope of this work.

We begin our analysis with a cluster of three gold atoms, which allows an investigation of a number of different bonding arrangements for the sulfur atom to the gold. Au<sub>3</sub>SCH<sub>3</sub> has an even number of electrons and thus has a spin moment equivalent to an even number of Bohr magnetons. However, recognizing that this gold cluster is a model for a fragment of much larger gold NP we have allowed for fractional occupation numbers. During the electronic self-consistency, smearing is used after 20 cycles, starting with a value of 0.27 eV and progressively decreasing by ten and one hundredth. In order to determine the lowest-energy geometry and the spin magnetic state, four possible high-symmetry structures were optimized for each of the low values of spin:  $\mu_s = 0, 1, 2, \dots$ . The results for  $\mu_s = 0$  and 1 are illustrated in figure 1—the other spin states produce even higher total energies. The input structures were taken in our calculations with one, two and three Au–S bonds to reproduce those geometries in the surfaces of the NPs; then they are fully relaxed. But the distances were not fixed and they were optimized because the adsorbates of thiols on gold can alter the Au–sulfur and Au–Au binding.

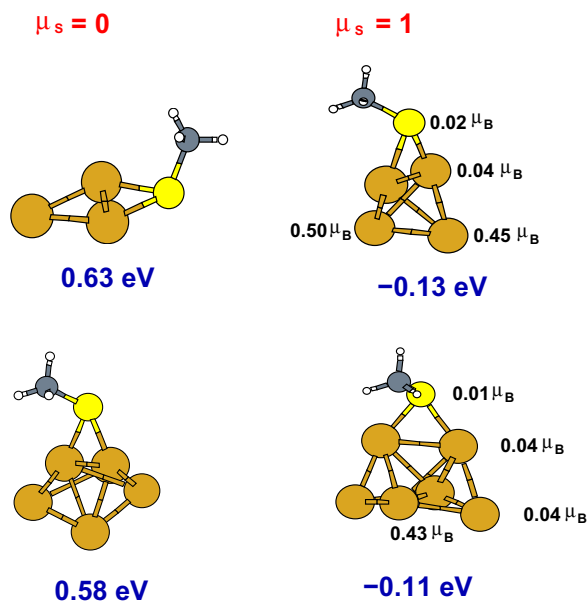
Calculations using DFT yield energies that depend on the approximate exchange–correlation functional used. In order to assess the qualitative validity of the calculated energies, structural sequence and spin states shown in figure 1, calculations with many other functionals, as implemented in ADF, were performed and shown in figure 2, using the fixed geometry



**Figure 2.** Splitting energy difference for many exchange-correlation functionals in  $\text{Au}_3\text{SCH}_3$ . We test the functionals ranging from local to meta-hybrid, separated by empty lines. See [15] and <http://www.scm.com/Doc/Doc2010/ADF/ADFUsersGuide/page90.html> for the acronyms concerning the functional notation.

obtained with the PBE GGA functional. The energy differences between different spin states were sometimes higher but never lower than that obtained with the PBE GGA functional. The other functionals produced energy differences of about 1.4 eV between the non- and spin-polarized structures. These supporting calculations confirm the main findings obtained using PBE: the bonding of an  $\text{SCH}_3$  molecule with a three-atom Au cluster has the zero total spin ground state structure depicted at the bottom of figure 1.

The calculated ground state structure has the thiol molecule in a bridge position and tilted with respect to the plane of the  $\text{Au}_3$  cluster. This ground state is 0.12 eV below the zero total spin configuration with the molecule in the  $\text{Au}_3$  plane. The total spin one states are significantly higher in energy. We are not aware of any previous investigation of this structural form of  $\text{Au}_3\text{SCH}_3$ . Although other molecules of Au-thiols have been studied previously [19], no report has been made of a model of the surface of gold NPs. Evidence for such a ‘tilt’ arrangement for the molecule was previously provided by [14] for thiols on gold metal surfaces. In addition, it has been suggested [14] that thiols could form a mat on a gold surface with perpendicularly oriented molecules. This would be the bridge position we have found with all the atoms bonded to S in the same plane, as shown in the third geometry of figure 1. However, this structure has a larger energy than the tilt case by 0.56 eV. Although this form links Au to S with a single

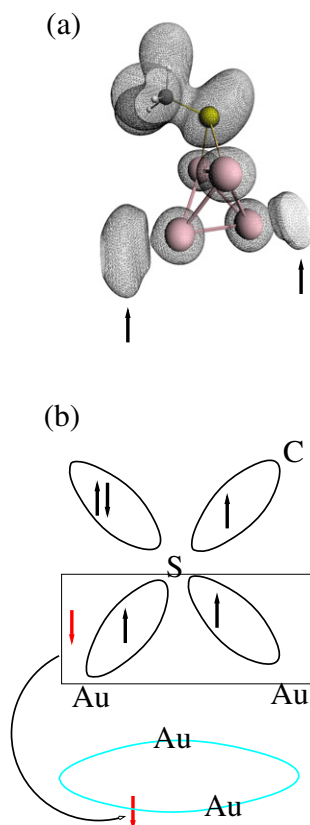


**Figure 3.** Relaxed structures for sulfur- $\text{Au}_n$  clusters. The numbers below the structures refer to the energetic difference between spin polarized and spin compensated structures. The numbers on the atoms refer to the local spin densities on the atoms for the ground states with spin polarization. Note that the odd-even oscillations in spin are shifted by 1 compared to the bare gold clusters.

bond, i.e., it has a similar coordination number to that of the studied cases of  $\text{C}_6\text{H}_5\text{-S-Au}_{13}$  [11, 12, 20], it is not considered in the results that follow because it is metastable, despite its spin polarization for alkanethiols.

The ground-state arrangements of other gold cluster structures are illustrated in figure 3. The panel on the left shows the structures with  $\mu_s = 0$  ground states, as previously discussed for the case of  $\text{Au}_3$ -thiol, whereas the right-hand panel shows clusters with spin polarization  $\mu_s = 1$ . The numbers shown below the structures give the energy difference in each case between the spin polarized and spin compensated states, which are almost independent of the size of the cluster. The energy differences  $\Delta E$  are around 0.5 and  $-0.2$  eV for the odd and even cases, respectively. These values should be considered to be estimates for the magnetic polarization, because the so-called orbital polarization is not included. However, it should be small as we are dealing with sp electrons. Most noteworthy is the shift in phase of the odd-even oscillations by a single gold atom with respect to pure gold clusters. The structure is spin compensated for an even number of gold atoms in the thiol cluster and spin polarized for an odd number.

This phase shift of the odd-even oscillations is not surprising in itself as the thiol bonded to the cluster has an odd number of electrons. However, the location of the magnetic moment is unexpected. Analysis of the electron distribution of the  $\text{Au}_n\text{SCH}_3$  clusters that contain an even number of gold atoms, and consequently an odd total number of electrons and a spin moment of 1, gives information on the distribution of magnetic moment which is shown in figure 3. The local magnetic moments of the thiols near the gold atoms are mostly negligible ( $<0.05 \mu_B$  per atom), while the moments of the lower gold atoms furthest from the thiol at  $\sim 0.5 \mu_B$  per atom are even higher than the experimental values. The spin moments are largely suppressed when



**Figure 4.** (a) Electron localization function for a cut-off value of 0.451. Note the attractors for electrons indicated by arrows. (b) Bonding mechanism of thiols on gold metal. The orbitals around the sulfur are four lobes like in  $sp^3$  configurations and the arrows indicate electrons from a sulfur atom. In order to form bonds with two gold Au atoms on a surface, a single  $sp$  electron must move to other gold atoms in the cluster.

the thiols would be located parallel to the gold surface. Depending on the orientation of the molecule, the spin moment varies due to different numbers of thiol–gold bonds.

Although some gold–thiol molecules were investigated both experimentally [1], and using *ab initio* calculations [9, 19], the behavior of their magnetic moment warrants further study. We have looked at the Au–S bond by means of topological analysis of the electron localization functions ELF [21]. By plotting ELF for isovalues between 0 and 1, we investigated the localization domains and basins for electrons. For  $ELF = 0.451$ , shown in figure 4(a), we see that the basins of Au–Au and Au–S bonds are separated. In fact, we observe an interesting attractor for electrons in the gold part (see the arrows). Figure 4(b) shows schematically the bonding mechanism of a thiolate on an Au cluster. A sulfur atom is shown here bonded to two Au atoms with a charge as given by  $sp^3$ -like hybridization. The spin population is smaller in these sulfur and bonded gold atoms than in the next-nearest neighbor Au atoms below the sulfur–gold bonds. There are five electrons in total directly participating in the chemical bonding with the sulfur: the two bonds with gold atoms share two electrons, an electron is shared in the bond with the carbon atom, and two more form a lone pair. Because each sulfur atom contributes



a total of six sp electrons, an electron is left over in the S–Au<sub>2</sub> bond and there must be sp electron transfer to the gold atoms below. It is this sp electron that contributes to the spin polarization on the gold counterpart.

This electron neutrality of sulfur with respect to the gold cluster is contrary to simple arguments based on electronegativity values and requires some investigation. We have estimated the Mulliken electronegativities  $M = (\text{IP} + \text{EA})/2$  of thiols and Au from our calculated ionization potentials (IPs) and electroaffinities (EAs). This  $M$  value is the negative of the electrochemical potential. The electronegativity of the SCH<sub>3</sub> unit is slightly higher<sup>5</sup> (5.43 eV) than the work function of about 5.22 eV for the Au surface [22] and is comparable with the  $M$  value for gold nanostructures ( $\lesssim 6$  eV) [23]. The SCH<sub>3</sub> unit behaves rather differently from the sulfur atom for which  $M = 6.21$  eV. Consequently, the transfer of charge from gold to sulfur cannot be assumed *a priori*. We looked at the charges in more detail. The d charges of gold remain the same in both pure and thiolate clusters, so the sp electrons are the relevant ones. The charge transfer of alkanethiol radicals is negligible (lower than 0.02e) when they bind to gold, i.e., sulfur atoms do not specially take charge. In fact, the Au atoms bonded to the sulfur atom lose sp charge (0.3e) to the gold atoms underneath. We stress that, independently of the partition scheme used, the calculated transfer of charge between the thiols and the gold clusters is much less than 0.1e. Such a charge neutrality is also seen in other systems, even in those assumed to be highly ionic [24], and supports the mechanism of back-donation with respect to sulfur previously mentioned.

We now compare our findings with those obtained from experiments on thiols and gold NPs. We stress that the sulfur atom is found not to be negatively charged, even though XANES experiments have shown that the 5d orbitals of gold are slightly open. The contribution to the magnetic signal of the sp electrons transferred to the gold is larger than the d orbital contribution. The donated electron from sulfur–gold bonds to gold atoms below also sits in the sp states of the Au cluster, and cannot be differentiated by the previous results using the XANES method. These sp electrons are almost free in the second gold layer and could orbit, and it is these that are responsible for the magnetism. These findings are consistent with experimental results in which a number of gold layers are needed in order to engender thiol-induced magnetism. This general picture is in agreement with the donor mechanism of carbon monoxide to Zn atoms on a ZnO surface [25] in that there is donation of a single electron from the molecule to the 4sp surface orbitals of Zn, which are initially empty. More importantly, it is also in agreement with the 4sp magnetism observed by XMCD in thiol-capped ZnO NPs [26].

Our results on thiolate–gold clusters can also be brought into contact with the magnetic data on larger particles. The method of application of thiols is via their deposition in layers on the surface of gold NPs. The magnetism that results should be that of the electrons induced by the capping molecules, which are confined to a thin layer below the gold surface. We have determined here the means by which this electron layer is open, giving rise to a permanent magnetic moment [27]. Orbital and spin moments are formed at the generally open Fermi level of the system, which is confined to a spherical shell under the gold surface. At the open Fermi level, the electronic levels are characterized by a collective magnetic moment that is rather similar to a giant atomic orbital, but with a much larger quantum number. The order of magnitude (0.1 or 0.01  $\mu_B$  per atom) is in agreement with that measured experimentally [1–5].

<sup>5</sup> Longer chains vary their electronegativity of the order of tens of eV; therefore our conclusion fully hold.

Although we have focused on thiol–Au clusters, copper–thiolates shows similar good bonding behavior with thiols. The related magnetic ground states have the same spin state ( $1 \mu_B$ ) and lie at similar energies with respect to the state with zero moment. This finding explains why recent experimental work carried out for these NPs [5] found ferromagnetic signals and deserves further investigation.

We have included the spin–orbit coupling along two directions: (i) parallel, along the Au–Au bond attached to sulfur, and (ii) perpendicular, in an axis starting from the middle point of such a bond towards the sulfur atom. The method of calculations is fully self-consistent. The energetic difference between both directions leads to magnetic anisotropies, MAE, of 1.43 and 0.98 meV per SCH<sub>3</sub> molecule for the Au<sub>4</sub> and Au<sub>6</sub> cases, respectively, while the change of MAE in the plane parallel to the surface is less than an order of magnitude. These results are comparable with the giant magnetic anisotropy of single cobalt atoms on a Pt surface (9 meV per Co atom) [28]. Such large values of MAE demonstrate the stability at room temperature of the magnetism discussed here, and are a factor of ten larger than the corresponding values for tetragonal Ni (0.2 meV). The results of a recent experiment [1] showed that the magnetism of gold NPs covered by thiols can indeed survive almost unchanged at room temperature, and it could therefore be used in hyperthermic applications.

In summary, we predict that the bonding of alkanethiols to gold clusters (i.e. SCH<sub>3</sub>Au<sub>n</sub>) results in a bridge arrangement with a deviated axis in a spin polarized ground state for even values of  $n$ . This structure is characterized by a division of functions, in that while the sulfur atom and the close pair of Au atoms are responsible for the chemical bonding, it is the subsurface gold atoms that host most of the magnetic moment. Thus, it should be possible for NPs of other noble metals to show similar magnetic behavior. Further avenues of investigation could include the fabrication of separated thiols on the surface of NPs, and the development of novel magnetic NPs for medical applications. We could also speculate that the extra electron in the gold particle at low coverages might help us to raise those atoms out of the surface as seen at high coverages for closed-shell gold cores [7–10].

## Acknowledgments

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